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Anomalous precipitation hardening in Al-(1 wt%)Cu thin films

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ABSTRACT

This paper concentrates on the precipitation hardening of Al-(1 wt%)Cu thin films. It is shown that in contrast to bulk, the well-known approach of precipitation hardening in confined systems like thin layers and thin films does not operate in the conventional way. This work analyses and discusses the precipitate hardening and its relation to the precipitation mechanism of Al-(1 wt%)Cu thin films which are subjected to precipitation hardening, nano-indentation hardness measurements. Microfabricated Al-(1 wt%)Cu thin films were solution treated at 550 °C for 15 min, quenched and aged at 190 °C for various durations up to 48 h. Nano-indentation hardness measurements revealed for the first time an unexpected decrease in hardness at just ~ 8 hours of aging, followed by a saturating increase. Microstructural analysis employing electron microscopy (high-resolution transmission, scanning, backscatter diffraction, energy dispersive spectroscopy) and x-ray diffraction revealed GP zones and θ precipitates but no θ' in as-received films, and only θ precipitates for aging durations longer than 6 h in the precipitate hardened films. Through-thickness analyses of aged specimens highlighted that θ precipitates nucleate and grow essentially at grain boundary grooves and at the specimen surface as preferential nucleation sites, while depleting Cu from the grain interior. It is shown that the growing precipitation at the surface and grain boundary grooves depletes the Cu in the thin film interior explaining the weakening-hardening sequence observed in the hardness measurements. Hence, the work shows that precipitation kinetics, and not thermodynamics, determine the precipitation state in thin films.

1. Introduction

The aluminum-copper alloy (Al-Cu) system, with copper as the solute element, is well known for its mechanical performance resulting from different metastable and stable Al_xCu_y precipitates that can co-exist, depending on composition and thermal history. This was already discovered in the early 1900 s by the German metallurgist Alfred Wilms [1], who observed that, at room temperature, quenched Al-(4 wt%)Cu hardens over a period of several days. By optimizing the heat treatment, efficient combinations of light weight and high strength properties are achievable. The Al-Cu alloy was therefore one of the first aluminum alloy systems to be employed in aerospace structures, such as the Wright flyer's crankcase [2] and later with its prime application in rigid airship frames in the 1920 s and 1930 s.

This advantageous precipitation behavior is not only exploited at the macroscale. Al-Cu thin films are applied in conducting wires in micro-electronics and mechanical structures in metallic micro-electromechanical systems (MEMS). This combines the desired electrical and microfabrication characteristics of Al, with the required resistance

against electro-migration and creep [3–5]. Also the main free path of moving and mobile dislocation densities were investigated using a combined pulse-nuclear magnetic and transmission electron microscopy approach in Al-Cu precipitation hardened thin foils [6]. Although this alloy improves device reliability from an electrical point of view, there are important concerns from a mechanical point of view. Recently, it was shown that Al-(1 wt%)Cu thin films, processed in a MEMS fabrication line, exhibit a significant time-dependent anelastic deformation recovery after unloading over a period of days [7,8]. It has been hypothesized that this behavior is related to the precipitation state [9,8]. Investigating the precipitation hardening behavior in these thin films is essential to assess possible deformation mechanisms relevant to MEMS device reliability.

The precipitation process is well understood for engineering applications of bulk Al-Cu [10–12]. The solubility of copper is only 0.1 wt% at room temperature, see Fig. 1(a). A copper concentration above the solubility limit is metastable, in which case the copper will segregate and eventually form stable Al_2Cu precipitates, i.e. the so-called θ phase. Despite the low Gibbs free energy of θ , its formation rate is quite

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Fig. 1. (a) (partial) equilibrium phase diagram of Al-Cu, where the solvus lines of GP1, GP2, and (dashed lines) and (solid line) denote the upper temperature limit of stability of the respective precipitate (reproduced from [11]). (b) Hardness measurements of bulk aluminum with different copper weight fractions, after homogenization at 550°C and aging at 190°C, showing a peak in hardness between and days of the final over-aged hardness depending on the copper fraction (reproduced from [11]).

small at room temperature due to its high interface energy, because the θ crystal structure is fully incoherent with the FCC aluminum matrix. Consequently, the formation of θ is often preceded, due to quenching procedures in heat treatments, by other smaller, metastable Al-Cu clusters with higher Gibbs free energy, but a lower interface energy: (I) nucleation in the matrix of nano-meter sized coherent Guinier-Preston zones, GP1 and GP2, which are ordered, solute-rich clusters of atoms; (II) formation of the much larger semi-coherent θ' precipitates mainly at GP zones or dislocations. The effect of this sequential precipitation mechanism on the Al-Cu material strength is shown in Fig. 1(b), depicting the hardness as a function of aging time, for a range of copper concentrations. For the considered aging temperature, an optimum in hardness, referred to as the peak-aged condition, is found between ~ 1 and ~ 10 days and reaches $>20\%$ of the final hardness of over-aged states, i.e. $t > t_{\text{peak-aged}}$ depending on the copper concentration. The presence of this peak is attributed to the prevalence of finely dispersed, semi-coherent θ' precipitates, whereas upon further aging weaker θ precipitates precipitate from/at θ' , grain boundaries and interfaces and grow at the expense of θ' resulting in a decrease of hardness [10].

In contrast to bulk metallic alloys, the precipitation hardening process in thin films and Al-Cu thin films in particular, has been studied to a lesser extent. Although precipitate hardening measured through nano-indentation appears similar as in bulk alloys [13], the precipitation sequence appears to be different. Most reports of thin film Al-Cu alloys only provide proof of the presence of θ -precipitates [4,14–17,13] or the absence of GP-zones or θ' [18], while only one report confirms formation of metastable phases in relatively Cu-rich (3 wt%Cu) Al-alloy thin films [19]. This does not clarify the precise precipitation sequence, and therefore does not enable a proper understanding of the precipitation hardening and creep mechanisms in thin films. Hence, the goal is to elucidate the precipitation mechanisms and its relation to precipitation hardening.

For this purpose, this paper presents a detailed investigation of the Al_xCu_y precipitation process in Al-(1 wt%Cu) thin films. This material system can be regarded as a model system for precipitation in thin-film (aluminum) alloys in general, because (i) its bulk counterpart is fairly well understood, and (ii) pure Al-Cu is relatively simple compared to typical engineering (aluminum) alloys, which contain a much larger variety of (semi-)coherent and incoherent precipitates. Therefore, the strategy is as follows. First, the hardness is characterized for a range of aging states, revealing an unexpected hardening evolution. The microstructure of the different precipitation states is thoroughly

characterized using a combination of high resolution transmission electron microscopy (HRTEM), wide angle x-ray scattering, scanning electron microscopy (SEM), electron backscatter diffraction (EBSD) and energy dispersive spectroscopy (EDS). These different microanalysis techniques substantiate that the hardness evolution is controlled by the precipitation state. Finally, hypotheses are formulated to explain the micro-structural origin of this evolution.

2. Materials preparation

A commercial micro-fabrication processing scheme, based on the PASSI process [20], is employed to make chips with free standing MEMS structures and films on substrate. The process includes a number of sequential patterning, deposition and etching steps on silicon wafers. For the present analysis, the following processing steps are important: (i) the plasma sputter deposition of pure Al-(1 wt%Cu) to a thickness of 5 μm at a substrate temperature of 450 °C, followed by an unforced cool-down to room temperature in air; (ii) after the Al-Cu deposition process, several deposition, wet etch and photolithography processes were performed to structure the free standing thin film. Temperatures varied between 50 °C and 400 °C in a time span of several minutes to an hour depending on the process. The last process step exposed the structures to temperatures of 50–60 °C for 10' s of minutes. The resulting 5 μm -thick Al-(1 wt%Cu) free-standing film is next referred to as the as-received film. Additionally, a similar processing scheme was employed [21] to produce free standing MEMS structures and films on substrate in pure Aluminum (99.99%), referred to as pure-Al.

Generally, heat treatments for Al-Cu alloys usually involve the following stages [11]: (i) solution treatment and homogenization at a temperature well above the θ solvus to dissolve all Al_xCu_y precipitates and uniformly distribute the Cu-solutes; (ii) rapid cooling or quenching usually to room temperature to obtain a supersaturated solid solution (α' phase); (iii) aging to enable controlled decomposition of the α' phase through subsequent formation of GP1, GP2, θ' , and θ precipitates.

Concerning stage (i), complete homogenization of Al-(1 wt%Cu), requires a temperature well above ~ 350 °C, see Fig. 1(a). Here, 15 min at 550 °C was used, based on the computed maximum required diffusion time for given diffusion length ($\sim 10 \mu\text{m}$) at this temperature, which results in negligible native oxide growth [22] or grain growth (further discussed below). Regarding stage (ii), submerged quenching in water results in mechanical deformation due to stiction of the free-standing MEMS structures to the underlying silicon chip, while

quenching in air is too slow. Therefore, an extended quenching procedure adopted based on the one proposed by Joo [23,16]: the silicon chip is placed on a thin layer of ethanol on a large cold polished block of copper. The ethanol layer greatly enhances the heat transfer, achieving a theoretical cooling rate of $\sim 300^\circ\text{C/s}$, while having a thickness less than half the chip thickness, which prevents wetting of the chip's surface. Finally, stage (iii) requires again an appropriate combination of aging time, t_{aging} , and temperature. An aging temperature of 190°C was chosen for three reasons: (I) it is well above the GP1 and GP2 solvi (see Fig. 1(a)), which excludes the formation of GP-zones and limits the type of expected precipitates to θ and θ' , thereby facilitating interpretation; (II) the θ' precipitates have the most significant contribution in hardening the material; (III) this temperature was also used in the hardness measurements of bulk Al-Cu in Fig. 1(b), which enables direct comparison. Two independent series of Al-(1 wt%)Cu MEMS structures were subjected to the proposed heat treatment, for which the temperatures were controlled to within 2% of the target temperature. The duration of the aging treatments ranged between 1 and 48 h.

3. Nanoindentation for characterization of precipitate hardening

An MTS XP nano-indenter in a controlled environment (pneumatic vibration isolation table, $T = 21 \pm 0.5^\circ\text{C}$) was operated under load-rate control. One set of specimens, with heat-treated, pure Al and Al-Cu as-received states, was loaded up to 20 mN at a rate of $dF/dt = 0.2\text{ mN/s}$ followed by a 10 s hold period and subsequently unloaded at the same rate down to 0.6 mN. The other set of specimens, with heat treated and as-received states, was loaded up to 250 mN, (at a rate of $dF/dt = 10\text{ mN/s}$), directly followed by unloading at the same rate down to 7.5 mN. Indentation depths did not exceed 500 nm, in accordance with the 10%-film thickness rule to exclude substrate effects. Chips were glued to aluminum stubs using superglue and excluding specimen tilt. Indentation sites were located on the thin metal film directly supported by the substrate. The (non-negligible) surface roughness was $R_a = 70\text{ nm}$. The high roughness motivates the application of a sufficiently high-load, resulting in relatively deeper indents and thus less influence of surface roughness. Measurements with a Berkovich tip reveal variations (not shown here) due to variations in indent position with respect to grain boundaries and due to surface roughness asperities. Therefore, a spherical indenter ($d = 250\text{ }\mu\text{m}$) was employed to exclude indentation size effects [24] and to reduce single asperity effects. This spherical indenter also enabled sufficiently large indentation zones with respect to grain size ($d_{\text{grain}} = 7\text{ to }14\text{ }\mu\text{m}$) at these loads to always include a few grain boundaries. The roughness also affects the indentation depth measurement, normally used to determine the contact area in hardness. To mitigate this effect, a hardness extraction procedure was adopted based on work by the group of Nix [25,26]. Under the assumption of known and constant reduced modulus throughout the indentation depth, the hardness H can be determined from the contact stiffness, while making the contact area, and hence indentation depth, redundant.

The indentation hardness H as function of aging at 190°C shows for both low ($\square$) and high ($\circ$) load a similar trend as function of duration, see Fig. 2. First of all, the hardness magnitudes of the low and high load indentation differ. This is attributed to the work hardening effect observable when indenting with spheres [24] and the difference in loading rate of two orders of magnitude [27]. When converting the magnitude of the high load indents to Vickers Hardness ($HV \sim H/0.0098 = 30$), these are comparable to extrapolated bulk values, see Fig. 1(b). The high load indents reveal smaller standard deviations than at low load, indicating the anticipated reduction of the influence of surface roughness. Furthermore, low load indentation of the as-received state ($\diamond$) revealed a hardness similar to the homogenized state: $H = 0.08\text{ GPa}$. Low load indentation of pure Al (∇) reveals $H = 0.06\text{ GPa}$, which is significantly lower than that of the Al-Cu alloys.

Fig. 2. Nano-indentation hardness measurement at two loads as a function of aging time for the Al-(1 wt%)Cu thin film after the same heat treatment as used for Fig. 1(b). The measurements show a decrease in the hardness instead of a peak, already at 8 h instead of days. For comparison, both a pure Al specimen and an as received Al-(1 wt%)Cu are analyzed.

Aging up to 6–8 h does not significantly change the initial hardness of 0.1 GPa and 0.33 GPa for, respectively, low and high load. From 8–10 h a decrease to 0.08 GPa (low load), respectively 0.23 GPa (high load) is observed, followed by an increase up to a plateau of 0.12 GPa (low load), respectively 0.3 GPa (high load). Interestingly, no significant peak-aged condition is observed. Although the hardness measurements for low load have relatively large spread, the trend of a hardness decrease and subsequent increase is significant as these are also observed for the measurements at high load with much smaller spread. This decrease-increase trend is different from bulk indentation, see Fig. 1(b): when extrapolating that data, no decrease and only a minor increase of hardness would occur only near 10 days of aging. In contrast, the results reported here suggest a precipitation effect with no or much less hardening that is faster in thin films than in bulk. To clarify this, further microstructural analysis of the thin-film Al_xCu_y precipitation mechanism is required. Based on the large change in hardness after $t_{\text{aging}} = 8\text{ h}$, artificial aging times of 0, 6, 8, 10, and 24 h were selected for further analysis of the precipitation state in addition to the as received state.

4. TEM Characterization of as-received Al-(1 wt%)Cu

A free-standing structure of the as-received film was analyzed by high-resolution transmission electron microscopy (HRTEM). Specimens were carefully prepared by subsequent ultrasonic cutting, polishing, dimpling, and precision ion polishing at 4 kV (PIPS system of Gatan). In contrast to focused ion beam milling, PIPS did not generate amorphous aluminum regions due to Ga-ion implantation. Subsequent high resolution imaging and electron diffraction analysis was performed with a JEM 2010F microscope operating at 200 kV, combined with energy-dispersive X-ray spectroscopy (EDS; 127 eV resolution, Bruker EDS system).

First, an EDS analysis of the aluminum matrix was performed (not shown). All peaks could be identified and correspond to Al or Cu, yielding concentrations of $(99.80 \pm 0.01)\text{ wt\%}$ and $(0.20 \pm 0.01)\text{ wt\%}$ for Al and Cu respectively, which is in agreement with values reported by Lokker et al. [18]. However, the copper concentration is noticeably lower than the average concentration of 1 wt% in the Al-Cu thin films.

Fig. 3. Transmission electron microscopy (TEM) images of the as-received Al-(1 wt%)Cu microstructure. (a,b) Dark field (DF) image of the aluminum matrix (obtained with the encircled reflection indicated in the diffraction pattern) showing many dislocation structures. (c, d) HRTEM Al[110] images of the lattice structure of Guinier-Preston zones, GP1 and GP2, as indicated by the arrows. (e,f,g,h) images of θ precipitates: (e) two θ precipitates at a grain boundary, (f) HRTEM enlargement of the largest precipitate, (g) selected area Al_2Cu [113] diffraction (SAD) pattern of this precipitate in which the Al_2Cu crystal structure is identified, and (h) dark field image obtained with the $\text{Al}_2\text{Cu}\{\bar{1}10\}$ reflection, for the same area as (e).

This indicates that most of the copper has migrated out of the probed region, e.g., to the top or bottom surface of the free-standing structure or its grain boundaries, which was also suggested by Lokker et al. [18].

Next, overview images of the aluminum matrix were made in bright and dark field TEM, together with diffraction patterns from the Al [111], Al[112] and Al[011] zones. Two of the dark field images are shown in Fig. 3(a) and (b) along with their diffraction patterns and the reflection used for the dark field images. These overview images consistently reveal a high density of dislocations, with pronounced dislocation structures, $\rho_d = \sim 130 \cdot 10^{12} \text{ m}^{-2}$ estimated using the method by John Steeds [28]. Dislocations appear because of thermal contraction during the cool down step after deposition. This contraction induces a biaxial tensile strain in the thin film well beyond the yield strain. Besides dislocations, many precipitates can be observed. Most of them are GP zones, which were identified in HRTEM Al[110] bright field images, as shown in Fig. 3(c) and (d). This chemical identification was

confirmed by local EDS analysis, which showed an increase in copper concentration at the GP zones. The HRTEM images clearly show that GP zones are coherent precipitates of a few nanometer in size, with GP2 being somewhat larger than GP1, in agreement with the literature [10]. Moreover, GP zones were observed throughout the aluminum matrix. Their presence is logical considering the final processing steps at elevated temperatures below the GP-solvi, see Fig. 1(a).

In addition to GP zones, θ precipitates were observed, as shown in Figs. 3(e)–(g). The θ crystal structure was positively identified from its atomic structure, shown in Fig. 3(f), and its selected area diffraction pattern, shown in Fig. 3(g). The random misorientation of the Al_2Cu diffraction pattern with the (faint) Al diffraction pattern, resulting from little aluminum material above or below the θ precipitate, shows that their orientations are uncoupled, as one would expect for fully incoherent precipitates. The dark field image in Fig. 3(h) also shows that the orientation of the large θ precipitate is unrelated to that of its

smaller neighbor. These θ precipitates reside on an aluminum grain boundary, as shown in Fig. 3(e). This is consistent with literature where θ precipitates in thin films are mainly found on grain boundaries and at interfaces [19,14,4,29,30,18]. However, a few nano-sized θ precipitates were also observed in the grain interior in these as-received specimens. The presence of these precipitates likely results from the relatively high temperatures for short time intervals to which the specimen was exposed during processing.

The most remarkable observation is the fact that one type of precipitate was not found at all: the θ' precipitates. Given the thermal history and taking into account that θ precipitates are identified, one would expect θ' precipitates to be present as well. Moreover, θ' precipitates principally nucleate at GP zones, dislocations and sometimes even grain boundaries (Ref. [31,19,11]), which were abundant in these specimens. One would therefore expect θ' precipitates that are finely dispersed over the aluminum matrix to be visible in this detailed TEM analysis. Nevertheless, it will be shown below that X-ray diffraction data also indicates the absence of θ' precipitates. It is therefore unlikely that the missing θ' precipitates are measurement artifacts. The absence of θ' precipitates might be related to the precipitation kinetics that is specific for these micromachined thin films: large dislocation densities and large surface/grain-boundary-to-bulk ratio may serve as enhanced diffusion pathways for Cu-solutes [10]. This absence is consistent with the absence of a pronounced hardness peak in Fig. 2 in contrast to bulk material (Fig. 1(b)).

5. Microstructural analysis of solution heat treated specimens

Before investigating the precipitation formation process, it was validated whether all alloying elements have dissolved without altering the grain size or grain structure. For this, a FEI Sirion FEG-SEM with EDAX OIM and EDAX EDS system with Apollo SDD detector was employed for backscatter electron (BSE) imaging, electron-backscatter diffraction (EBSD) and EDS. BSE imaging was performed with $E_{\text{beam}} = 15$ kV. EBSD was collected with $E_{\text{beam}} = 20$ kV., with a step size of $0.5 \mu\text{m}$. EDS was measured with $E_{\text{beam}} = 20$ kV.

First, a chain of the largest θ precipitates, which were identified at a particular grain boundary, were compared before and after the solution treatment, see Fig. 4. EDS analysis of the copper concentration shows that even these largest θ precipitates fully dissolved into the matrix, while Cu redistributed homogeneously over the matrix (compare Fig. 4(b) with (c)). Moreover, no traces of other elements besides aluminum and copper were found after homogenization, therefore, the material is not contaminated during the heat treatment.

Additionally, a detailed map of crystal orientations and grain boundaries was acquired before and after solution treatment. Figure 5(a) shows a top view specimen image of a free-standing MEMS

Fig. 4. The effect of the homogenization step at 550°C on the precipitate state in the as-received Al-(1 wt%)Cu material. (a) back-scatter electron (BSE) image of large θ precipitates (with sizes up to half a micrometer) aligned on a grain boundary. (b,c) EDS maps of the copper concentration (b) before and (c) after the solution heat treatment, revealing full dissolution of the copper.

structure that was imaged with electron back-scatter diffraction (EBSD). No grain boundary migration, nor grain growth can be observed after the solution treatment at 550°C . It is therefore unlikely that grain growth occurs in the subsequent aging heat treatment at 190°C . Furthermore, it was analyzed whether systematic spatial variations in the (average) grain structure for different positions on the wafer exist due to thermal gradients during previous processing. To this end, large portions of the wafer were imaged using light microscopy, see Fig. 5(b), whereby it was found that the grain size was smaller near the wafer edge. Subsequent EBSD analysis showed that the grain size at the wafer center and edge is, respectively, $(14 \pm 6) \mu\text{m}$ and $(7 \pm 3) \mu\text{m}$, of which Fig. 5(c) gives an example. Moreover, EBSD consistently shows that the Al-(1 wt%)Cu thin films have a pronounced Al(111) texture, i.e. the vast majority of crystals have their $\langle 111 \rangle$ axis aligned within 20° to the surface normal. To exclude grain size effects, all further analyses were performed on specimens obtained from the wafer center.

6. Microstructural analysis of aged specimens

X-ray diffraction (XRD) spectroscopy was performed to identify the precipitates present at aging times of 0, 6, 8, 10 and 24 h. Specimen preparation consisted of transferring the Al-(1 wt%)Cu thin film MEMS structures from the silicon substrate by embedding in a thin layer of cyanoacrylate glue. After solidification of the glue it formed a thin foil suitable for XRD. Preliminary XRD 2-theta line-scan measurements using a powder diffractometer did not reveal the expected precipitates. The absence of diffraction peaks may be caused by a preferential texture of the precipitates or a limited amount of precipitates of random orientation in the measurement volume, through which diffraction peaks can be missed in an XRD line scan. Therefore, 2D wide-angle X-ray diffraction (WAXD) patterns were obtained at the European Synchrotron Research Facility, see Fig. 6(a)–(e). Measurements were performed at the BM26B DUBBLE beam line: beam diameter of ~ 5 mm; wavelength of 0.1033 nm; CCD detector with resolution of 1024^2 and $97.65 \mu\text{m}^2$ pixels positioned at a distance of ~ 75 mm. Specimens were mounted in transmission configuration with the surface normal parallel to the X-ray beam. To facilitate interpretation, radial diffraction plots were obtained by (i) azimuthal integration of the intensity rings in the WAXD patterns of Fig. 6 and (ii) subsequent subtraction of the corresponding specimen-specific glue background spectrums (e.g. Fig. 6(f)). This procedure yielded the five radial intensity spectra shown in Fig. 7.

All five specimens show a strong Al(111) reflection at $2\text{-theta} = 25.50^\circ$ and a smaller Al(200) reflection at $2\text{-theta} = 29.50^\circ$, whereby the latter is only observed for $t_{\text{aging}} = 8$ h and $t_{\text{aging}} = 10$ h specimens, see Figs. 6 and 7. This large difference in peak intensity is due to the predominant Al(111) texture, also observed with EBSD in Fig. 5, whereas the few individual reflections on the Al(200) ring in Fig. 6(c) and (d) indicate the presence of a few crystals that have a large misorientation relative to the Al(111) texture within the ~ 5 mm broad X-ray beam. Indeed, 3D-orientation calculations show that the predominant Al(111) texture with its misorientation spread within $\sim 20^\circ$, favoring the Al(111) reflection, which is strongest for crystals with a misorientation of the $\langle 111 \rangle$ axis to the surface normal of $\sim 8^\circ$. The Al(200) reflection on the other hand is optimal for an angle of the $\langle 111 \rangle$ axis to surface normal of $\sim 40^\circ$. Crystals with such a large misorientation could not be observed in the three EBSD images in Fig. 5 and are likely rare.

Besides these aluminum peaks, only two other reflections, at $2\text{-theta} = \sim 27.5^\circ$ and $\sim 28^\circ$, were identified above the noise level, and only for aging times of 10 h and especially 24 h. These two reflections do not correspond to aluminum or θ' reflections. Instead, they are attributed to the $\text{Al}_2\text{Cu}\{220\}$ and $\text{Al}_2\text{Cu}\{122\}$ reflections of the θ precipitates, even though their positions are shifted to a somewhat lower angle compared to the tabulated spectrum of bulk Al_2Cu . This shift would correspond to a tensile strain of $\sim 0.5\%$ in the θ precipitates, which may be realistic since these precipitates preferentially grow in

Fig. 5. (a) electron back-scatter diffraction (EBSD) measurements of a free-standing MEMS structure before (a1) and after (a2) the solution treatment of 15 min at 550 °C, for which no grain boundary motion could be observed (the black areas are openings in the free-standing structure, introduced for under-etching these structures to remove a sacrificial layer during processing). (b) Examples of optical images, obtained at the edge (b1) and at the center (b2) of the wafer, which were used to investigate systematic differences in grain size over the wafer. Etching during previous processing attacked the grain boundaries, making these optically visible (broad lines). The small inset shows an overview of a set of 20 µm-wide free-standing cantilevers. (c) Example of an EBSD image of a cantilever with anchor, which was used to analyze grain sizes and grain boundaries. The colors in figures (a) and (c) indicate the local crystal orientation according to the inverse pole figure color map shown in the inset, indicating a pronounced Al(111) texture of the grains in the Al-(1 wt%)Cu thin films.

the grain boundary grooves at the surface, as discussed below, where surface tension is high [32]. This case may be comparable to the tensile stress that develops in the island-coalescence regime in thin film deposition [33]. Moreover, the smooth shape of the $\text{Al}_2\text{Cu}\{122\}$ ring in azimuthal direction indicates that a considerable fraction of θ precipitates was present in the X-ray beam. However, even though TEM analysis (Fig. 3) revealed θ precipitates that are fully incoherent with the aluminum matrix, the $\text{Al}_2\text{Cu}\{122\}$ ring in the WAXD spectra of Fig. 6(d) and (e) reveals a pronounced preferential orientation related to the growth at the surface and in grain boundary grooves. This preferential orientation explains the mismatch in the ratio of the $\{220\}$ to $\{122\}$ intensities compared to the tabulated bulk Al_2Cu spectrum, as well as the absence of the two other expected Al_2Cu reflections (i.e. the $\theta\{211\}$ and $\theta\{222\}$ reflections at, respectively, $2\theta \approx 25^\circ$ and $\sim 37^\circ$). These latter reflections could also be eclipsed by, respectively, the nearby Al $\{111\}$ reflection and the large noise level close to the end of the detector range at $2\theta \approx 38^\circ$.

Finally, it is striking that none of the three θ' reflections (i.e. the $\theta'\{200\}$, $\theta'\{103\}$, and $\theta'\{202\}$ reflection at, respectively, $2\theta \sim 20^\circ$, $\sim 34^\circ$, and $\sim 36^\circ$) were observed for any of the five specimens. As θ' precipitates nucleate in the Al-Cu bulk at GP zones or dislocations, they are expected to be finely-dispersed over the aluminum matrix [11], whereby their concentration was expected to be noticeably larger than that of θ precipitates. Especially the absence of the strong $\theta'\{103\}$ reflection is surprising. Because of their semi-coherent nature, θ' precipitates have their $[001]$ axis parallel to Al $[001]$ [11]. Therefore, the strong Al $\{111\}$ texture considerably affects the orientation distribution for θ' if present. 3D-orientation calculations indicate that half of the θ' population should be favorably oriented for the $\theta'\{103\}$ reflection, which is strongest for aluminum crystals with a misorientation of the $\langle 111 \rangle$ axis to the surface normal of $\sim 10^\circ$. Therefore, taking into account a misorientation spread of $\sim 20^\circ$ of the Al $\{111\}$ texture, the strong $\theta'\{103\}$ reflection should be present if θ' precipitates exist in the aluminum matrix. Yet, the θ' reflections are absent, which is consistent with the TEM observations. The absence of θ' precipitates may explain the absence of the peak in hardness with respect to bulk Al-Cu, suggested in Section 4.

More insight in the formation of θ precipitates may be gained by measuring the copper concentration over the film thickness as a function of aging time. To this end, focused ion beam milling was used to make slanted cross-sections of the aged free-standing films, after which back-scatter electrons (BSE) images and EDS-Cu images were measured to investigate the evolution of the copper concentration, see Fig. 8. BSE images were obtained with $E_{\text{beam}} = 10$ kV and EDS mapping was performed with $E_{\text{beam}} = 5$ kV., resulting in $d_{\text{X-ray volume}} \approx 0.5 \mu\text{m}$. Note that only copper clusters above a few tens of nanometers exceed the EDS noise level, which are θ precipitates, because θ' has been ruled out and GP zones are not present at an aging temperature of 190 °C. In the BSE images also smaller precipitates can be identified, whereas precipitates in roughness valleys are only partially visible.

Now let us first examine the evolution of the θ precipitates on the top surface. As already discussed above (Fig. 4(c)), after homogenization, the copper concentration is homogeneously distributed. After 6 h of aging, a few surface precipitates are observed (encircled in yellow), while the average Cu-concentration in the grain/film interior is ~ 0.97 wt%. With only 2 and 4 additional hours of aging, many more and larger precipitates appear at the surface, as visible in the BSE images, and it becomes apparent that most of them are located in a grain boundary groove (GBG), while the average Cu-concentration in grain/film interior reduces to ~ 0.90 wt%. For the 24 h specimen, the average Cu-concentration in grain/film interior further reduces to ~ 0.50 wt%, while an increasing number of precipitates are found at the surface, however, the increase of the precipitate size has saturated. Conversely, the internal θ precipitates, which are observed from the cross-section, follow an opposite trend. At 6 and 8 h of aging, two internal precipitates were found in the film interior and all four of them were located at a grain boundary. However, the two precipitates of the 6 h specimen are larger than their 8 h aging counterparts, and from 10 h aging onward no precipitates are found anymore in the grain interior. This indicates that the few θ precipitates that have nucleated on the internal grain boundaries within the first 6 h of aging, gradually disappear upon further aging. Although θ precipitates are thermodynamically stable, they may dissolve due to two mechanisms: (i) small precipitates may dissolve to facilitate the growth of a few large precipitates to reduce the

Fig. 6. raw 2D wide-angle X-ray diffraction (WAXD) patterns, for Al-(1 wt%)Cu MEMS structures, heat treated at 190 °C for (a) 0, (b) 6, (c) 8, (d) 10, and (e) 24 h, and subsequently transferred from their underlying substrate to cyanoacrylate(glue) foils. For each aging state, Al-Cu-on-glue and glue-only diffraction pattern were recorded, where the (nearly amorphous) glue showed a few minor reflections attributed to polymer crystallization, see, e.g., (f). Indicated in the images are the most pronounced diffraction rings of aluminum, θ precipitates, and glue.

system's precipitate-matrix interface energy, so called Ostwald ripening [10]; (ii) if energetically more favorable nucleation sites are present within the copper diffusion length, e.g. free surface or GBGs, a net copper-flux to these lower-energy sites may occur and trigger nucleation. Both mechanisms seem to be active as discussed next.

7. Discussion

Summarizing the main observations: (a) no significant peak-aged condition is found in the hardness measurements of these films; (b) a minimum in hardness is observed at relatively short aging duration; (c) the θ' precipitates are absent in the detailed TEM analysis of the as-

Fig. 7. Radial X-ray diffraction spectra of Al-(1 wt%)Cu, heat treated at 190 °C for $t_{\text{aging}} = 0, 6, 8, 10$, and 24 h, where the radial diffraction intensity is obtained by (i) azimuthal integration of the intensity rings in the 2D WAXD patterns of Fig. 6. and (ii) subtraction of the corresponding glue background spectrums. For clarity, the spectra are vertically shifted with increasing aging time. Reference positions of reflections that are pronounced enough to surpass the noise level are indicated by solid, dashed, and dotted vertical lines for, respectively, aluminum [35], θ precipitates [36] and θ' precipitates (calculated using hkl -indices from [37] and d -spacing values from [10]). The theoretical relative intensity between reflections of the same crystal is indicated between the brackets with a maximum of 999.

received material and in the WAXD analysis of aged specimens; (d) θ precipitates appear already after 6 h and are strongly present after 10 h. Other investigations of thin film Al-Cu of similar composition do not reveal the presence of θ' either [18]. It may therefore be concluded that θ' precipitates are absent in these Al-(1 wt%)Cu thin films for these heat treatments. Furthermore, the fast occurrence of a hardness minimum and appearance of θ precipitates would be in line with reported observations that θ precipitates form at lower temperatures than suggested by the phase diagram of bulk Al-Cu [18]. The results reveal that the precipitate hardening behavior is different from its bulk counterpart. The precipitation is anomalous as θ' is not part of the precipitation sequence at the investigated temperature. It is hypothesized that the large free surface-to-volume ratio and large grain-boundary-to-volume ratio of these thin films is causing this. The fact that the hardness has a minimum, is hypothesized to result from two competing precipitation mechanisms: one mechanism with decreasing influence upon aging and a second one with an increasing influence.

7.1. Anomalous precipitation

The following hypothesis explains the absence of θ' and the relatively fast occurrence of θ in the thin film compared to the bulk alloy. Most θ precipitates nucleate directly in a GBG, without evolving from θ' , because GBGs are the energetically most favorable locations for θ to nucleate in these thin films. This implies that the total defect energy, of GBG and precipitate, is reduced inside a GBG, by partially relaxing the high surface tension that exists in GBGs [32,33]. After nucleation of θ precipitates at GBGs the growth of these precipitates is kinetically controlled by the diffusion of Cu atoms from the grain interior and grain boundaries. In these thin films, the kinetics is facilitated by grain boundaries, as well as by dislocations in the as-received material as a result of thermal stresses during processing. The hypothesis that the total defect energy is smaller than in the bulk alloy may explain a number of observations: (i) it causes a net flux of copper atoms from θ precipitates on internal grain boundaries to θ precipitates in GBGs, i.e. explaining the gradual disappearance of the former θ precipitates after ~ 8 hours of aging; (ii) it favors θ nucleation, since it induces a larger reduction in free energy than θ' nucleation in the aluminum matrix; (iii) it triggers a higher θ nucleation rate in GBGs than in the bulk, justifying

the faster appearance of θ in Al-(1 wt%)Cu thin films (only ~ 8 hours) compared to the bulk Al-(1 wt%)Cu alloy (more than ~ 10 days), see Fig. 1(b)). Note that the free surface is expected to have a less strong, yet similar role as the GBGs in (i)-(iii). Hence, the GBGs and free surface are energetically and kinetically more favorable for Cu to diffuse to and precipitate as θ , thus preventing the nucleation of θ' and reducing the θ precipitation in the bulk of the film.

7.2. The hardness minimum

The following hypothesis explains the observed hardness minimum in the nano-indentation measurement on these Al-(1 wt%)Cu thin films. First of all, the absence of θ' precipitates explains the absence of a peak in hardness that is observed in bulk Al-Cu (Fig. 1(b)). Interestingly, the hardness measurements of specimens in as-received state, shown to contain GP-zones, and solid-solution reveal similar hardness as that of pure aluminum, which can be explained by the fact that the influence of copper solutes and coherent GP zones on dislocation motion has been reported to be similar [34]. With increasing aging time, copper can easily diffuse to the surface, using the internal grain boundaries as fast diffusion pathways, where θ precipitates start to nucleate in the GBGs already after a couple hours. These, however, are not expected to affect the indentation hardness, because their presence at the surface does not obstruct the dislocation motion in the interior. Also, the effect of the few small θ precipitates on the internal GBs observed at $t_{\text{aging}} = 6$ h is expected to be negligible. At the same time the Cu-solute concentration of the grain interiors decreases with increasing aging time, resulting in a decreasing effect on the hardness and the minimum around $t_{\text{aging}} = 10$ h. In contrast, the θ precipitates at the surface not only increase in number, but also grow to a considerable size due to Ostwald ripening [10]. In the absence of other microstructural changes that contribute to hardening, i.e. very low Cu-concentration, no GP zones or θ' precipitates, unchanged grain boundary structures, the only explanation for the observed minor increase in hardness in Fig. 2 just after $t_{\text{aging}} = 10$ h is traditional precipitate hardening: θ precipitates at GBs and free surface form sufficiently large obstacles to dislocations that tend to escape from the surface, triggering dislocation pile-ups at these precipitates and subsequently dislocation networks in the sub-surface area. After 24 h aging, the size of the surface precipitates stabilizes, which is consistent with the saturation in hardness for large aging times.

8. Conclusions

The precipitation (hardening) mechanism of Al-(1 wt%)Cu thin films was investigated by nano-indentation, high-resolution TEM, SEM, EBSD, EDS and WAXS analyses and heat treatment variations, i.e. as-received specimens of microfabricated thin film structures were subjected to a solution treating at 550 °C and artificial aging at 190 °C up to 48 h to create a well defined precipitation state without GP zones. Nano-indentation hardness measurements did not show a peak-aged condition as found in bulk Al-Cu. Instead, a small decrease in hardness at ~ 8 hours was observed, followed by a slow increase and saturation at ~ 20 hours. Therefore, it is noted that a precipitation hardening treatment is not advisable for this thin film Al-Cu alloy for use in e.g. MEMS applications.

The detailed microstructural analysis did reveal the expected presence of GP zones (only in as-received material) and θ precipitates were present. However, θ' was not observed at all, suggesting that precipitation of θ' must be highly unfavorable in thin films. Through-thickness measurements of aged specimens highlighted that θ precipitates nucleate sooner than expected and grow essentially at grain boundary grooves, and to lesser extent the specimen surface, at the expense of the interior of the thin film. Therefore the following hypothesis was proposed to explain the absence θ' and the relatively fast nucleation of θ . Precipitation of θ is favored at grain boundary grooves

Fig. 8. (left and center) BSE images of slanted cross-section of (different) free-standing 5 μm -thick Al-(1 wt%)Cu structures, artificially aged for different t_{aging} . Precipitates are encircled in yellow and magnified in the center column. (right) EDS images of the copper concentration, corresponding to the region in the orange box on the BSE images. For each EDS map, also the averaged copper concentration of the film interior is noted, where the error margin indicates the uncertainty of the mean value, excluding possible systematic error that are expected to be equal for all these specimens. From top to bottom, image pairs (a,b), (c,d), (e,f), and (g, h) correspond to $t_{\text{aging}} = 6, 8, 10$, and 24 h aging at 190 $^{\circ}\text{C}$. The cross-sectional EDS-Cu plot of $t_{\text{aging}} = 0$ h (not shown) is completely homogeneous, in agreement with Fig. 4(c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

and surfaces, because these locations are energetically favorable nucleation sites. Simultaneously, precipitation kinetics reduce Cu solutes from the interior of the thin film thus limiting θ' and θ precipitation in the interior. The depletion of Cu in the thin film interior also reduces the effect of Cu solute hardening. This combined Cu-depletion θ precipitation mechanism explains the anomalous precipitation hardening trend.

Even though considerations of thermodynamic equilibrium energy suggest various phases of precipitates could be present, this work shows that the precipitation kinetics determines the precipitation state in these thin films. The reduced length scales in thin films make precipitation kinetics the determining factor for the precipitation state of thin films. Thus microstructure engineering of thin film alloys should take kinetics into account.

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